PATENT SPECIFICATION

NO DRAWINGS

1,104,467

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Date of Application and filing Complete Specification: June 23, 1965.
No. 26538/65.
Application made in United States of America (No. 379397) on June 30, 1964.
Complete Specification Published: Feb. 28, 1968.

Index at acceptance:—C3 C(1B1, 1E1, 1E2); C3 P(11C17, 11C20D2, 11D5, 11F2, 11T2B)
Int. Cl.:—C 08 f 47/08

COMPLETE SPECIFICATION

ERRATA

SPECIFICATION No. 1,104,467

Page 1, line 17, *for* "to" *read* "do"
Page 1, line 30, *for* "production" second occurrence *read* "product"
Page 2, line 29, *for* "formed" *read* "foamed"
Page 3, line 46, *after* "of" *insert* "a"

THE PATENT OFFICE
4th September 1968

ERRATUM

SPECIFICATION No. 1,104,467
Amendment No. 2

Page 1, line 30, *after* "of" *insert* "a"

THE PATENT OFFICE
14 October 1968

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SEE ERRATA SLIP ATTACHED

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COMPLETE SPECIFICATION

Production of Cellular Oxymethylene Polymers

We, CELANESE CORPORATION (formerly known as Celanese Corporation of America), of 522 Fifth Avenue, New York, 36, State of New York, United States of America, a company incorporated in accordance with the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of cellular products from oxymethylene polymers.

Various polymeric materials are now available as cellular products. Some such products are of a soft, spongy texture and to not possess great physical strength but are useful as padding in upholstery and in other applications where resilience is needed. Other such products are of a rigid nature and find their chief applications as insulating materials for restricting the passage of heat or sound or for protection against damage of articles packed in them; these latter products are not usually very resistant to crushing and when crushed lose much of their ability to insulate or protect.

The present invention is concerned with the production of cellular production which, although possessing in some at least of its forms a degree of resilience, is, in general, notable for its toughness and resistance to crushing and is made of a normally solid oxymethylene polymer.

The cellular product may be made from an oxymethylene homopolymer such as may be obtained, for instance, by polymerising formaldehyde or trioxane and the polymer may be end-capped with ether or ester groups to increase its terminal stability. Preferably, however, the product is made from an oxymethylene copolymer having distributed among the oxymethylene groups forming the major part of the polymer molecules other groups having adjacent carbon atoms which form links in the polymer chains. Such polymers can be obtained in a very satisfactory manner by copolymerising trioxane with from 0.4 to 15 mole per cent of a cyclic ether having adjacent carbon atoms in its molecule such as, for instance, ethylene oxide or 1,3-dioxolane. These copolymers are of greater thermal stability than the homopolymers and can be given remarkably high thermal stability by controlled thermal or hydrolytic degradation so as to eliminate terminal oxymethylene groups. Whether an oxymethylene copolymer or homopolymer is used its thermal stability may be enhanced with the aid of chemical stabilisers, especially a combination of an antioxidant and an anti-scission agent, e.g. a substituted bisphenol together with a compound containing trivalent nitrogen.

According to the invention, the conversion of the oxymethylene polymer into a cellular product of the "closed-cell" type is effected by forming a foam of the polymer in liquid form and a gas having no deleterious effects on the polymer at the temperature used and then solidifying the polymer. It has been found that a satisfactory product can be obtained without the aid of a supplementary foaming agent or gas by using as the gas formaldehyde generated by decomposition of oxymethylene polymer. Thus a copolymer of the type referred to above but from which the terminal oxymethylene groups have not been removed may be heated in a closed vessel to melt the polymer and generate formaldehyde by removing the terminal oxymethylene groups, and the pressure then reduced so that the polymer and gaseous formaldehyde form a foam which is then cooled to obtain the cellular product. Again, oxymethylene homopolymers degrade easily under the action

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SEE ERRATA SLIP ATTACHED

and slip number 2

of heat, especially in presence of a base, and the cellular product may be formed with the aid of formaldehyde gas generated by heating a copolymer, even one from which terminal oxymethylene groups have been removed, together with an oxymethylene homopolymer and, preferably, with a base. The base may be produced *in situ* during heating by forming the original mixture from copolymer, homopolymer and a compound which is decomposed by heat to liberate a base. It should be noted that the copolymers referred to are resistant to the effect of bases and do not decompose when heated with them to temperatures which cause rapid decomposition by a base of oxymethylene homopolymers.

In using this method, the polymer may be heated initially to a temperature, for example, in the range of 230 to 300°C. and under a gauge pressure of at least 75 pounds per square inch for a period of, for example, 30 to 45 minutes to cause substantial generation of formaldehyde gas. The heating is preferably conducted in an inert atmosphere, e.g. of nitrogen or argon. The partially degraded polymer may then be transferred to a mould under atmospheric pressure, so that the resulting liberated formaldehyde gas causes the polymer to assume a formed structure, and then cooled. Alternatively, the molten polymer may be confined in a mould during the initial heating step and the pressure regulated to a level which will cause the generation of gas to form a shaped foamed structure directly without transferring the molten polymer under pressure to a mould at a lower pressure. The mould mav be heated by such methods as the use of electrical heating elements or a heat transfer medium such as, for example, hot oil or superheated steam.

However, the molten polymer may be converted into a foamed product by physically mixing it with a gas supplied from an external source, the gas used being one which is substantially inert to the polymer at the temperature of the molten polymer, for example nitrogen, argon, carbon dioxide, helium, neon, krypton, xenon, methylene chloride, carbon tetrafluoride and fluoro-carbons. Various types of commercial machinery may be used to foam the polymer with the inert gas. For example, sigma blade and paddle type mixers can be used to disperse the inert gases which are injected through valved jets into the body of the molten polymer under high pressure. The inert gas may be preheated to preserve the polymer in molten condition while it is being formed into a foamed structure. Moreover, the injection of inert gas may be carried out under elevated pressure so that the gas initially dissolves somewhat in the molten polymer and is liberated when the pressure is released.

Another method of foaming the oxymethylene polymer with a gas is to mix the polymer with a conventional foaming agent and then heat the mixture to a temperature high enough to melt the polymer and to liberate the foaming gas from this agent. Some foaming agents which may be used are azodicarbonamide, azobisisobutyronitrile, benzenesulphonylhydrazide, diazoaminobenzene, N,N′-dimethyl-N, N′-dinitrosoterephthalamide, dinitrosopentamethylenetetramine, 4,4′-diphenyldisulphonylazide, and 4,4′-oxybis (benzenesulphonylhydrazide). The foaming agent may be used, for example, in an amount of 0.5 to 20 weight per cent based on the weight of the polymer. This method of foaming may be carried out directly in a mould to form specific foamed shapes directly.

The following Examples illustrate the invention. Except in Example 3 the oxymethylene copolymer used is one produced from trioxane and 2 weight per cent ethylene oxide and stabilised by removal of the terminal oxymethylene groups and also by the addition of 0.1% of cyanoguanidine and 0.5% of 2,2′-methylene bis-(4-methyl-6 tertiary butyl phenol).

Example 1

Particles of the oxymethylene copolymer are mixed with 2 weight per cent of N,N′-dinitrosopentamethylenetetramine and are placed in a mould which is then closed. The mixture is agitated in the mould which is heated to a temperature of approximately 180°C. At this temperature the polymer becomes molten and the foaming agent generates a gas. The mould is then cooled to room temperature and, upon opening the mould, a foamed structure of the "closed-cell" type is found which in some instances has a hollow interior.

The foamed oxymethylene copolymer can be shaped by moulding in a mould heated to approximately 180°C.

Example 2

The oxymethylene copolymer and 2 weight per cent of azodicarbonamide are loaded into a mould and tamped to completely fill the mould. The mould is then closed, placed in a pressure clamp and heated to a temperature of approximately 180°C, to melt the polymer and activate the foaming agent. The mould is then cooled to room temperature and opened. A shaped foamed structure of the "closed-cell" type is obtained.

Example 3

The oxymethylene copolymer used is one which has not been stabilised by removing the terminal oxymethylene groups. This material is placed in a mould using a mould pressure of approximately 500 pounds per square inch and a temperature of 230°C. Under these conditions the polymer partially degrades by removal of its comparative unstable terminal

oxymethylene groups, until carbon-to-carbon bonds are reached in the polymer chains, with liberation of gaseous formaldehyde which acts as the foaming agent. After the mould is cooled the polymer is removed and is found to have a porous structure of the "closed-cell" type.

EXAMPLE 4

The oxymethylene copolymer is heated in an autoclave equipped with paddle mixers to a temperature of 200°C. After 5 minutes at this temperature, nitrogen is injected into the molten mass at a pressure of 100 pounds per square inch by means of jets. The mixture of molten polymer and gas is beaten into a foam by the paddle mixers. The foam is then removed from the mixture and is placed in cooling trays to form slab stock or into moulds to form appropriate structures. The foams produced by this method are normally of the "closed-cell" type.

EXAMPLE 5

The oxymethylene copolymer is dissolved in butyrolactone at a temperature of 145°C. and mixed with N,N′-dinitrosopentamethylenetetramine as foaming agent. The mixture is then solidified by cooling to room temperature to yield a raw moulding material having a foaming agent widely and uniformly dispersed therein. This material is then moulded at a temperature of approximately 190°C., at which temperature the copolymer is molten, and results in a foamed structure having "closed-cell" structure.

EXAMPLE 6

0.5 gram of guanidine carbonate is dissolved in approximately 40 millilitres of water and the solution filtered through fine filtering paper. A small amount of acetone is added to the solution to act as a wetting agent. The solution is mixed with 45 grams of the oxymethylene copolymer to form a slurry which is allowed to dry in a hood for three hours and then placed in a vacuum oven for 36 hours at a temperature of approximately 50°C. 5 grams of commercial esterified oxymethylene homopolymer are added to this mixture which is then plastographed at 30 revolutions per minute in a nitrogen atmosphere at a temperature of 188°C. for five minutes. After cooling this material is ground to particles which pass through a 40-mesh screen. This material is then heated at a temperature of 220°C. to cause liberation of guanidine which attacks the homopolymer, causing evolutions of formaldehyde gas. A foam results in three minutes.

The above Examples all produce foamed cellular structures having densities between 0.3 and 1.35 grams/cc. approximately, with "closed-cell" cavities having average diameters between 0.0001 and 0.1 inch approximately. The cavities comprise between 5 and 80% of the volume of the oxymethylene polymer.

Foamed articles made by the above methods are useful as heat and sound insulation materials, for making a wide variety of items, e.g. light-weight seats, arm rests and crash pads, self-lubricating light-weight bearings and moulded toys, and for electrical dielectric applications such as potting materials and wire spacers.

WHAT WE CLAIM IS:—

1. Process for the production of a cellular product of the "closed-cell" type, which comprises forming a foam of an oxymethylene polymer in liquid form and a gas having no deleterious effects on the polymer at the temperature used and then solidifying the polymer.

2. Process according to Claim 1, wherein the oxymethylene polymer used is one having distributed among the oxymethylene groups forming the major part of the polymer molecules other groups having adjacent carbon atoms which form links in the polymer chains.

3. Process according to Claim 2, wherein the polymer contains, as said other groups, 0.4 to 15 mole per cent of oxyethylene groups.

4. Process according to Claim 1, 2 or 3, wherein the gas used is formaldehyde generated *in situ* by thermal degradation of the oxymethylene polymer.

5. Process according to Claim 1, 2 or 3, wherein the gas used is formaldehyde generated *in situ* and the polymer used is a mixture of an oxymethylene homopolymer and an oxymethylene copolymer and the generation of formaldehyde from the homopolymer is facilitated by the presence of a base.

6. Process for the production of a cellular product of the "closed-cell" type from an oxymethylene polymer, substantially as hereinbefore described.

7. Process for the production of a cellular product of the "closed-cell" type from an oxymethylene copolymer, substantially as described in any of the Examples.

8. Cellular products of the "closed-cell" type made from oxymethylene polymers, whenever obtained by any of the processes claimed in Claims 1 to 7 and articles made therefrom.

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